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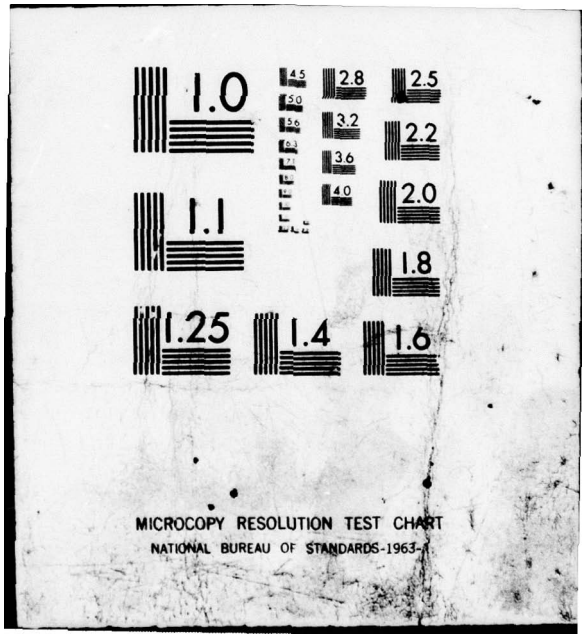
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AN INVESTIGATION OF THE DYNAMICAL PROPERTIES OF CRYSTALS BY RAMAN SPECTROSCOPY

Final Technical Report

by

W. Taylor

June 1979

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United States Army

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This report describes light scattering measurements from a variety of materials which undergo structural phase transitions. The materials studied include boracites, lead germanate and perovskites and the studies have found new transitions, determined the nature of the soft mode and detailed the changes in the spectra due to the presence or additon of impurities. In addition associated theoretical work has questioned the validity of the usual way of interpreting soft mode results obtained from light scattering techniques.

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An experiment was also performed to study the light scattering from magnons in a mixed antiferromagnet.

Abstract

This report describes light scattering measurements from a variety of materials which undergo structural phase transitions. The materials studied include boracites, lead germanate and perovskites and the studies have found new transitions, determined the nature of the soft mode and detailed the changes in the spectra due to the presence or addition of impurities. In addition associated theoretical work has questioned the validity of the usual way of interpreting soft mode results obtained from light scattering techniques. An experiment was also performed to study the light scattering from magnons in a mixed antiferromagnet.

Table of Contents

1. Introduction

Light scattering is a powerful technique for the study of the excitations in crystals. We have used it to study the behaviour of the excitations close to structural phase transitions. In this report we briefly describe the results which have been found on a variety of systems. Detailed accounts of this work have in most cases been published or are about to be published.

In addition to these results work has also been performed on developing the light scattering techniques. This has partly been in the field of improving the computer programmes for running the Raman scattering experiments and associated data analysis, but also considerable effort has been devoted to building a very stable Fabry Perot interferometer. The instrument is now nearly complete and we hope will be operational soon.

2. Results

(i) Boracites ($M_3B_7O_{13}X$, where M = metal and X = halogen)

Boracites, in general, undergo a complicated sequence of structural phase transitions when cooled from the high-temperature cubic phase. The first transition is of an improper ferroelectric type, where the primary order parameter is a displacement of a zone-boundary mode. On further cooling there are frequently more structural transitions which in some instances lead to ordered magnetic structures where the magnetic and ferroelectric polarisations are coupled and may be simultaneously switched by external fields.

In the course of this programme we have studied two examples of the boracites, namely $Cu_3B_7O_{13}C\ell$ and $Ni_3B_7O_{13}I$ (which we call "Cu-Cℓ" and "Ni-I" boracites for convenience).

Cu-Cℓ boracite is the most nearly continuous of all the boracites and therefore of most interest with regard to the critical properties of improper ferroelectrics. On the other hand, Ni-I boracite exhibits the most interesting magnetic behaviour becoming simultaneously antiferromagnetic and ferroelectric at 64 K with also a broad maximum in the magnetic susceptibility near 100 K.

Boracite crystals are not easy to work with, the samples are not only very small, but are also highly coloured and this severely limits the choice of the laser excitation wavelength.

We have studied Cu-Cℓ boracite[1] at various temperatures above and below the cubic-orthorhombic transition at 365 K. Many new bands appear in the Raman spectrum at T_c as expected but the most interesting finding is the identification of two A-symmetry soft modes in the ferroelectric phase. Above T_c the A_1 symmetry spectrum exhibits the Rayleigh wing feature common to all boracites and not yet explained. In our much more exhaustive study of Ni-I boracite[2,3,4,5] we postulate some kind of disorder as the cause of this low-frequency scattering. The measurements on Ni-I were extended down to very low temperatures using a liquid helium cryostat and several new and interesting observations were made. Most important of these, was the discovery of a new transition at 7 K. Spectra recorded over the

range 6 K to 300 K show that there are anomalies in the mode-frequencies and damping at 128 K, 68 K and 7 K. The anomalies at 68 K coincide with the known 1st-order ferroelectric transition. In the region of 128 K there is a broad maxima in the dielectric constant and magnetic susceptibility together with an 0.1% increase in the lattice constant. However there is no other evidence for a phase transition at this temperature. Maxima in the Rayleigh intensity and the appearance of new modes clearly demonstrate the existence of transitions at both 68 K and 7 K.

(ii) Barium-doped lead germanate ($Pb_{5-x}Ba_xGe_3O_{11}$)

The replacement of only a small percentage of the lead atoms in lead germanate by barium has a dramatic effect on the ferroelectric properties; for only 5.6% Ba the value of T_c falls by nearly 100 K from 450 to 358 K. We have studied in detail corresponding changes in the Raman spectra[6] and we find that apart from increased damping, all modes other than the soft-mode are comparatively unaffected by the barium doping. The temperature dependence of the ferroelectric soft mode is however strongly affected and this suggests that the lead atoms are directly involved in the soft mode motion.

The soft mode is connected with a very intense quasi-elastic or central peak scattering which occurs close to the ferroelectric transition at 450 K. In earlier work we had shown the central peak to be predominately static in origin, possibly as a result of impurity effects. Thus the deliberate addition of impurities

such as barium might be expected to have a pronounced effect on the central peak. The reliable measurement of central peak intensities is difficult since the effect of varying absorption in different samples has to be taken into account. The results indicate[7] however that barium doping enhances the static central peak intensity and that it occurs over a larger temperature range than in the pure material. This result shows that defects do give rise to a central peak but the origin of the static central peak in nominally pure samples is still an open question. Attempts to make detailed measurements on the dynamic central peak in pure lead germanate have been delayed by the difficulty of obtaining adequate stability in the Fabry Perot interferometer but we hope this experiment will be performed soon.

(iii) Lead germanate - soft-mode line-shape analysis[8,9]

A long and exhaustive series of computer-fitting procedures was carried out on the ferroelectric soft mode spectra of pure lead germanate using various different models. The most successful fit was obtained with a response function which includes a term to describe coupling with phonon density fluctuations. However this model predicts a lifetime for the phonon density fluctuations which is larger than expected and we are forced to conclude that this discrepancy is caused by a basic deficiency in the theory.

Most recently a re-examination of this problem was carried out on the initiative of Professor Y. Yacoby and this work[8] suggests that close to T_c there is an appreciable contribution to the

Raman scattering arising from the interference terms between the one- and two-phonon processes. Our work suggests that these interference terms might be large at all structural phase transitions at which the soft mode is not Raman active above T_c. The interference terms give rise to a change in the lineshape. If the lineshape is then analysed in terms of the normal one-phonon spectral functions the values of the mode frequencies and line widths are then incorrect. If these conclusions are correct much of the Raman scattering work close to structural phase transitions must be reinterpreted.

(iv) Perovskites[10] ($SrTiO_3$)

Strontium titanate is regarded as the archetype of materials in which a (neutron-scattering) central peak has been found. Despite this no definitely equivalent peak has been observed in light scattering. The same situation holds for other members of this perovskite class.

We acquired (from H.J. Scheel) a supposedly very perfect crystal of $SrTiO_3$ and tried repeatedly to find a central peak in the light scattering spectrum, but without success. The discrepancy between the light and neutron scattering results is still not understood.

At the same time, in order to determine the purity or otherwise of this particular sample we recorded in detail its Raman spectrum in both the cubic and tetragonal phases for comparison with another supposedly less perfect sample. As a result we found clear evidence of impurity-induced one-phonon modes in various samples. This, together with a careful analysis of the results

of neutron scattering and infrared work has allowed us to present a much more detailed analysis of the zone-centre modes in $SrTiO_3$ than any previously published. Results on the isomorphous materials $RbCaF_3$ and $KMnF_3$ were also presented.

(v) $KMn_xNi_{1-x}F_3$ - magnetic excitations

The mixed crystal $KMn_{1-x}Ni_xF_3$ is a disordered antiferromagnet and as such its Raman spectrum might be expected to contain both one and two-magnon effects. Four samples (with $x = 0.84$, 0.73; 0.54 and 0.15) were studied at temperatures from 9 to 300 K and three temperature-dependent peaks due to two-magnon scattering were observed.[11] The scattering is attributed to two-magnon excitations on nickel-nickel manganese-nickel and manganese-manganese ions respectively. Application of an Ising-cluster model yields the frequencies of the peaks in reasonable agreement with the experimental results, but the intensity of the Mn-Mn band is much less than expected. We suggest this is because the light scattering occurs from a near resonant process on the Ni ions.

(vi) Other Materials

Certain other materials were mentioned in our original research proposal which have not so far been referred to in this report:

(i) Potassium selenate (K_2SeO_4) - This material is of particular interest as it passes through an incommensurate phase. During consideration of our research proposal several other laboratories commenced work on the material performing

very similar experiments to those we had planned. In the interest therefore of avoiding duplication we decided not to proceed with work on K_2SeO_4.

(ii) Molecular crystals No work specific to this programme was carried out although a small group under Dr. G.S. Pawley at Edinburgh is carrying forward a parallel programme on molecular crystal dynamics.

(iii) Defective semiconductors ($Hg\square In_2Te_4$) This work was completed prior to the commencement of this programme.

3. Conclusion

The powerful technique of light scattering spectroscopy has been employed to study phenomena related to structural phase transitions in several quite different types of materials. Very different types of information have been obtained by these studies: for example new phase transitions have been found, soft modes discovered, and impurities shown to have a pronounced effect on the dielectric magnetic and dynamic properties of the materials. These observations are useful in the development of the understanding of the mechanism of the various kinds of phase transitions and in understanding and predicting the effects of doping and disorder. Such basic understanding of solid state mechanism is likely to be invaluable both to academic scientists and device engineers alike.

Future work in this area is likely to concentrate on the problems of impurities and disorder. Further progress on the "central peak" problem is likely to result from improved experimental techniques and better materials preparation.

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